(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 235 836 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of the patent specification: 29.11.89

(51) Int. Cl.[4]: C07H 13/06, C11C 3/12

(21) Application number: 87200138.3

(22) Date of filing: 30.01.87

(54) **Fatty acid esters of sugars and sugar alcohols.**

(30) Priority: 19.02.86 NL 8600415

(43) Date of publication of application: 09.09.87 Bulletin 87/37

(45) Publication of the grant of the patent: 29.11.89 Bulletin 89/48

(84) Designated Contracting States: AT BE CH DE ES FR GB GR IT LI NL SE

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(84) Designated Contracting States: BE CH DE ES FR GR IT LI NL SE AT

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(84) Designated Contracting States: GB

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Description

The present invention relates to fatty acid esters, in particular fatty acid polyesters of sugars and sugar alcohols (SPE). Such polyesters are known. Their preparation is described in, for example, US patent specifications 3,963,699 (G.P. Rizzi & H.M. Taylor), 4,517,360 (R.A. Volpenhein) and 4,518,772 (R.A. Volpenhein) and European patent specification 0 062 565 (Blohorn S.A.).

In general the SPE derived from saturated fatty acids with 12 or more carbon atoms are solid and the SPE derived from unsaturated fatty acids are liquid at ambient temperature.

In US patent specification 3,600,186 (F.H. Mattson & R.A. Volpenhein) the use is described of SPE having at least 4 fatty acid moieties per sugar or sugar alcohol moiety as low calorie fats in cooking and salad oil.

The use of SPE in fat-containing compositions is also described in US patent specifications 4,005,195 (R.J. Jandacek), 4,005,196 (R.J. Jandacek & F.H. Mattson), 4,034,083 (F.H. Mattson), 4,241,054 (R.A. Volpenhein & R.J. Jandacek), 4,264,583 (R.J. Jandacek), 4,382,924 (K.G. Berling & T.G. Crosby), and 4,446,165 (B.A. Roberts), whereas their use in a dietary beverage emulsion is described in US patent specification 4,368,213 (E.J. Hollenbach & N.B. Howard).

In this specification by "sugars and sugar alcohols" is meant a group of polyols having from 4 to 8 hydroxyl groups. Examples of preferred polyols are sugars, including monosaccharides and disaccharides, and sugar alcohols as well as derivatives thereof having from 4 to 8 hydroxyl groups.

Examples of monosaccharides having 4 hydroxyl groups are arabinose, ribose and xylose. An example of a sugar alcohol having 4 hydroxyl groups is the sugar alcohol derived from erythrose, i.e. erythritol.

Examples of monosaccharides having 5 hydroxyl groups are galactose, fructose, glucose and sorbose. An example of a sugar alcohol having 5 hydroxyl groups is the sugar alcohol derived from xylose, i.e. xylitol.

Examples of sugar alcohols having 6 hydroxyl groups are those derived from glucose and sorbose as well as from the hydrolysis products of sucrose, e.g. sorbitol and mannitol.

Examples of disaccharides are maltose, lactose and sucrose, the latter being preferred, all of which contain 8 hydroxyl groups.

Another example of a polyol having 4 hydroxyl groups is alpha-methyl glucoside (= alpha-methyl ether of glucose) which in fact is a sugar derivative.

As described in the above-mentioned publications, it is desirable that for polyesters being substantially non-digestable by human beings at least 4 hydroxyl groups are esterified. These non-digestable polyesters are not absorbed by the human body and therefore suitable for use in low-calorie compositions.

For many applications, including margarines and other fat spreads as well as cooking oils, the oxidative stability can be a limiting factor for practical use. In particular oxidative rancidity can occur with fats and oils products, which rancidity is formed via intermediates like peroxides leading to breakdown products of which aldehydes and ketones are the most important for the organoleptic quality of the fat product.

It is customary to use antioxidants in oil and fat products containing triacylglycerols (= triglycerides) based on natural fatty acids, both in pure and partially hydrogenated form to avoid autoxidation of the double bonds in the fatty acids radicals present in the oil and fat products.

It has now been found that the oxidation stability of SPE containing unsaturated fatty acid residues can be improved by providing the SPE with an effective amount of trans-unsaturated fatty acid chains.

In accordance with the present invention such effective amounts of trans-unsaturated fatty acid chains in the SPE can be derived from triacylglycerols or the corresponding fatty acids or lower alkyl esters thereof, which are hydrogenated under isomerizing conditions.

In "Fatty Acids" by K.S. Markley (Krieger publishing, 1983) the sucrose ester of alpha-eleostearic acid (cis-9-trans-11-trans-13-octadecatrienoic acid) is disclosed. This concerns a conjugated polyunsaturated system.

After trans-hardening to cis:trans double bond levels within the ranges in accordance with the present invention the polyester unsaturated fatty acid residues are substantially all mono-unsaturated.

Trans-hardened oils such as soybean oil and rapeseed oil which after trans-hardened have a melting point of about 36°C are preferred as fatty acid starting materials for the preparation of the SPE. Alternatively, the trans-hardening can be carried out with SPE-containing cis-mono- or cis-poly-unsaturated fatty acid chains as a starting material.

The polyesters according to the invention preferably have a ratio of cis:trans double bonds ranging from (20:80) to (40:60), more preferably from (30:70) to (35:65).

Good results were obtained with polyesters in which the ratio of cis:trans double bonds was that belonging to the thermodynamic equilibrium obtained by hydrogenating, under isomerising conditions which are known to the man skilled in the art of fat chemistry (see for example Bailey's Industrial Oil and Fat Products, Edited by D. Swern 3 (1964) 88–89 and 1053–54).

The effective amount can be determined by simple experiments using an accelerated oxidation test, whereby the product is subjected to aeration at a temperature of about 100°C. Such a test can be carried

out by an equipment marketed under the name of Rancimat ® by the firm Metrohm A.G., Herisau (Switzerland).

For the determination of the oxidative stability of oils and fats several methods have been developed in the past. One of these methods is the so-called Swift test. In this test a sample of oil is kept at about 100°C and at regular intervals the peroxide value is determined. The Induction Period (IP) is the time required for the Peroxide Value to reach an arbitrary value: for animal fats 20 and for vegetable fats 100 meq. oxygen per kg of fat. Since this method was labour-intensive and time-consuming, an automated version of the test was developed: the Rancimat. With the Rancimat the end of the IP is determined by the rise in conductivity of water, in which air is entrapped that has passed through the heated fat, thus carrying over low molecular weight acids, mainly formic acid, formed as breakdown product of peroxides. Rancidity itself is not measured with this test, because rancidity is only to be experienced organoleptically. However, good correlation has been found between flavour scores as determined by a panel and the IP determined with the Rancimat, for example for groundnut oil heated for 20 hours at 100°C with samples for analysis being taken every 2 hours.

In practice, both the Swift test and the determination of the Induction Period with the Rancimat give a good indication for the oxidative stability of an oil or fat under normal use conditions, both at ambient temperature and at cooking and frying temperatures. It is preferred that the SPE have a Rancimat value of at least 20 hours, more preferably at least 30 hours.

The following Table gives some values determined with the Rancimat test (I.P. ^{100} in hours).

Table

Polyol	Fatty acid type	Induction period	Melting point
<u>Saturated</u>			
s	BO65	at least 70[1]	60+
s	PK39	at least 70[1]	22.5
s	PO58	at least 70[1]	n.d.
s[2]	(1:3 w/w) PK39/PO58	at least 70[1]	48.5
g	AR[3]	at least 70[1]	60+
<u>Cis-unsaturated</u>			
s	AR	2–7	liquid at room temp.
s	BO	less than 1	
s	MZ	1	
s	OV	2–3	
s	SF	less than 1	
g	AR	less than 1	
<u>Mainly trans-unsaturated</u>			
s	BO36	at least 90[1]	22.7
s	RP36	36	24.7
s[4]	BO36/PO58 (1:2 w/w)	at least 115[1]	49.5
s[4]	BO36/PO58 (1:1 w/w)	80	43.0
s[4]	BO36/PO58 (2:1 w/w)	at least 115(1)	38.7
g	BO36	at least 95[1]	20.5

[1] After the hours given the experiment was interrupted; the oil was still stable at that time

[2] Saccharose fatty acid polyesters derived from a mixture of methyl esters of fatty acids derived from fully hydrogenated palmkernel oil (PK39) and fully hydrogenated palm oil (PO58)

[3] The arachidic oil fatty acids polyester of alpha-methyl glucoside was fully hydrogenated

[4] Saccharose fatty acid polyesters derived from a mixture of methyl esters of fatty acids derived from trans-hardened soybean oil (BO36) and fully hydrogenated palm oil (PO58)

Polyol: s = Saccharose (= sucrose)
Polyol: g = Alpha-methyl glucoside (= alpha-methyl ether of glucose)

The fatty acid type "saturated" means fatty acids derived from fully hydrogenated triglyceride oils, e.g. soybean oil (BO65), palmkernel oil (PK39) and palm oil (PO58). The numbers give the slipmelting point of the hardened oils.

RP36 = Rapeseed oil trans-hardened to a melting point of 36°C
BO36 = Soybean oil trans-hardened to a melting point of 36°C
AR = Arachidic oil
BO = Soybean oil
MZ = Maize oil
OV = Olive oil
SF = Sunflower oil

The Table shows that SPE's from saccharose and alphamethyl glucoside containing fully hydrogenated fatty acids have a high oxidative stability (Rancimat figures of more than 70 hours), whereas those polyesters of unhardened fatty acids derived from natural oils (fatty acid type "cis-unsaturated") have a poor oxidative stability (Rancimat figures of less than 1 up to 7 hours).

The SPE's from saccharose and alpha-methyl glucoside containing trans-hardened oils (fatty acid type "mainly trans-saturated") also have a good oxidative stability (Rancimat figures of 36 up to more than 115 hours). This good oxidation stability is considered surprising, since these polyesters, which are all liquid or semi-liquid at body temperature, still contain a relatively high proportion of unsaturated fatty acid radicals.

In the SPE's mentioned in the Table at least 75% of the hydroxyl group are esterified.

The SPE according to the invention having a high degree of esterification, e.g. SPE of which at least 50% or more than 70% or even more than 80% of the hydroxyl groups are esterified with fatty acids are preferred, since they can be used in food compositions or pharmaceutical compositions for decreasing the blood cholesterol level in human beings.

In order to improve the properties of the SPE as a fat substitute it is desirable that the fatty acid chains have at least 6 carbon atoms,preferably at least 8 carbon atoms and more preferably at least 10 carbon atoms. For practical purpose the fatty acid chains have at most 24 carbon atoms, preferably at most 20 carbon atoms. When natural oils and fats are used as starting materials for the fatty acids the latter have usually chains of from 12 to 22 carbon atoms.

The invention further provides the use of the SPE according to the invention in edible compositions containing 0.5-99 wt.%, preferably 10-99 wt.%, more preferably 30-80 wt.% of SPE according to the invention, the balance consisting of edible matter. Examples of such compositions are edible fat products suitable as a bread spread, as a baking, cooking or frying product, as a salad oil, or as pharmaceutical carrier.

Although the invention was mainly illustrated with sugar polyesters, the beneficial effect of the trans-unsaturated fatty acid residues can also be obtained when used in sugar esters containing only one, two or three fatty acid residues. Such sugar esters having a lower degree of esterification can be applied as emulsifiers, e.g. in the food industry. The lower part of the ranges given in the previous paragraph is of importance when the sugar ester is used as an emulsifier, whereas the upper part of the ranges is important when the sugar ester is used as a low-calorie fat substitute.

Claims

1. Fatty acid esters of sugars and sugar alcohols having from 4 to 8 hydroxyl groups, at least 20% of the fatty acid residues in said esters being unsaturated, characterised in that said unsaturated residues are substantially all mono-unsaturated, having a ratio of cis:trans double bonds ranging from (20:80) to (40:60).

2. Esters according to claim 1, in which at least 50%, preferably at least 70%, and more preferably at least 80% of said hydroxyl groups are esterified with fatty acids.

3. Esters according to claim 1 or 2, in which the degree of esterification is so high that the polyester is substantially non-digestible by human beings.

4. Esters according to any of the claims 1 to 3, which are esters of sucrose.

5. Esters according to any of the claims 1 to 4, comprising fatty acid chains having at least 6 carbon atoms, preferably at least 8 carbon atoms, more preferably at least 10 carbon atoms.

6. Esters according to any of the claims 1 to 5, comprising fatty acid chains having at most 24 carbon atoms, preferably at most 20 carbon atoms.

7. Esters according to any of claims 1 to 6, comprising fatty acid chains having from 12–22 carbon atoms.

8. Esters according to any of claims 1 to 7, in which the fatty acid chains are derived from triacylglycerols or the corresponding fatty acids or lower alkyl esters thereof, which are hydrogenated under isomerizing conditions.

9. Esters according to claim 8, in which said fatty acid chains are derived from trans-hardened rapeseed or soybean oil having a melting point of about 36°C.

10. Esters according to any of the claims 1 to 7, having a ratio of cis:trans double bonds ranging from (35:65) to (30:70), preferably a ratio of cis:trans double bonds belonging to the thermodynamic equilibrium obtained by hydrogenation under isomerizing conditions.

11. Esters according to any of the claims 1 to 7, comprising an amount of trans-fatty acids such that the product has a stability of at least 20 hours, preferably at least 30 hours in an accelerated oxidation test, whereby the product is subjected to aeration at a temperature of about 100°C.

12. A composition containing 0.5 to 99 wt.-%, preferably 10 to 99 wt.-%, more preferably 30 to 80 wt.-%, of esters according to any of the claims 1 to 11, the balance consisting of edible matter, which composition is preferably an edible fat product suitable as a bread spread, as a baking, cooking or frying product, as a salad oil, or as a pharmaceutical carrier.

Patentansprüche

1. Fettsäureester von Zuckern und Zuckeralkoholen mit 4 bis 8 Hydroxylgruppen, wobei mindestens 20% der Fettsäurerester in diesen Estern ungesättigt sind, dadurch gekennzeichnet, daß diese ungesättigten Reste im wesentlichen alle mono-ungesättigt sind und ein Verhältnis von cis:trans-Doppelbindungen im Bereich (20:80) bis (40:60) haben.

2. Ester nach Anspruch 1, in welchen mindestens 50%, vorzugsweise mindestens 70% und insbesondere mindestens 80% dieser Hydroxylgruppen mit Fettsäuren verestert sind.

3. Ester nach Anspruch 1 oder 2, in welchen der Grad der Veresterung so hoch ist, daß der Polyester für einen Menschen praktisch nicht verdaulich ist.

4. Ester nach irgendeinem der Ansprüche 1 bis 3, die Ester von Saccharose sind.

5. Ester nach irgendeinem der Ansprüche 1 bis 4, umfassend Fettsäureketten mit mindestens 6 Kohlenstoffatomen, vorzugsweise mindestens 8 Kohlenstoffatomen, insbesondere mindestens 10 Kohlenstoffatomen.

6. Ester nach irgendeinem der Ansprüche 1 bis 5, umfassend Fettsäureketten mit höchstens 24 Kohlenstoffatomen, vorzugsweise höchstens 20 Kohlenstoffatomen.

7. Ester nach irgendeinem der Ansprüche 1 bis 6, umfassend Fettsäureketten mit 12 bis 22 Kohlenstoffatomen.

8. Ester nach irgendeinem der Ansprüche 1 bis 7, in welchen die Fettsäureketten von Triacylglycerinen oder den entsprechenden Fettsäuren oder Niedrigalkylestern derselben abgeleitet werden, die unter Isomerisierungsbedingungen hydriert werden.

9. Ester nach Anspruch 8, in welchen die Fettsäureketten von trans-gehärtetem Raps- oder Sojaöl mit einem Schmelzpunkt von etwa 36°C abgeleitet sind.

10. Ester nach irgendeinem der Ansprüche 1 bis 7 mit einem Verhältnis von cis:trans-Doppelbindungen im Bereich von (35:65) bis (30:70), vorzugsweise einem Verhältnis von cis:trans-Doppelbindungen, das zum thermodynamischen Gleichgewicht, erhalten durch Hydrierung unter Isomerisierungsbedingungen, gehört.

11. Ester nach irgendeinem der Ansprüche 1 bis 7, umfassend eine derartige Menge der trans-Fettsäuren, daß das Produkt eine Stabilität von mindestens 20 h, vorzugsweise mindestens 30 h, in einem beschleunigten Oxidationstest hat, wobei das Produkt bei einer Temperatur von etwa 100°C einer Belüftung unterworfen wird.

12. Zusammensetzung, die 0,5 bis 99 Gew.-%, vorzugsweise 10 bis 99 Gew.-%, insbesondere 30 bis 80 Gew.-%, der Ester nach irgendeinem der Ansprüche 1 bis 11 enthält, wobei der Rest aus eßbarem Material besteht und die Zusammensetzung vorzugsweise ein Speisefettprodukt ist, das als Brotaufstrich, als Back-, Koch- oder Bratprodukt, als Salatöl oder als pharmazeutischer Träger geeignet ist.

Revendications

1. Esters d'acides gras de sucres et d'alcools de sucres contenant de 4 à 8 groupes hydroxyle, au moins 20% des restes d'acides gras dans lesdits esters étant insaturés, caractérisé en ce que lesdits restes insaturés sont pratiquement tous mono-insaturés, ayant un rapport des doubles liaisons cis:trans compris entre 20:80 et 40:60.

2. Esters selon la revendication 1, dans lesquels au moins 50%, de préférence au moins 70% et, mieux encore, au moins 80% desdits groupes hydroxyle sont estérifiés avec des acides gras.

3. Esters selon la revendication 1 ou 2, dans lesquels le degré d'estérification est tellement élevé que le polyester est pratiquement non digérable par les êtres humains.

4. Esters selon l'une quelconque des revendications 1 à 3, qui sont des esters de saccharose.

5. Esters selon l'une quelconque des revendications 1 à 4, comprenant des chaînes d'acides gras contenant au moins 6 atomes de carbone, de préférence au moins 8 atomes de carbone et, mieux encore, au moins 10 atomes de carbone.

6. Esters selon l'une quelconque des revendications 1 à 5, comprenant des chaînes d'acides gras qui contiennent au maximum 24 atomes de carbone et, de préférence, au maximum 20 atomes de carbone.

7. Esters selon l'une quelconque des revendications 1 à 6, comprenant des chaînes d'acides gras de 12 à 22 atomes de carbone.

8. Esters selon l'une quelconque des revendications 1 à 7, dans lequel les chaînes d'acides gras proviennent de triacylglycérol ou d'acides gras correspondants ou de leurs esters alkyliques inférieurs, qu'on hydrogène dans des conditions d'isomérisation.

9. Esters selon la revendication 8, dans lesquels lesdites chaînes d'acides gras proviennent de l'huile de colza ou de soja transdurcie ayant un point de fusion d'environ 36°C.

10. Esters selon l'une quelconque des revendications 1 à 7, ayant un rapport des doubles liaisons cis:trans compris entre 35:65 et 30:70, de préférence un rapport de doubles liaisons cis:trans appartenant à l'équilibre thermodynamique qu'on obtient par hydrogénation dans des conditions d'isomérisation.

11. Esters selon l'une quelconque des revendications 1 à 7, comprenant une quantité telle d'acides trans gras que le produit possède une stabilité d'au moins 20 heures, de préférence d'au moins 30 heures dans un test accéléré d'oxydation, dans lequel on soumet le produit à une aération à une température d'environ 100°C.

12. Composition contenant de 0,5 à 99% en poids de préférence de 10 à 99% en poids et, mieux encore, de 30 à 80% en poids d'esters selon l'une quelconque des revendications 1 à 11, le complément étant constitué de matières comestibles, composition qui est avantageusement une graisse comestible, avec laquelle on peut tartiner le pain et qui peut servir comme produit de cuisson au four, de cuisson ou de friture, en qualité d'huile à salade ou comme véhicule pharmaceutique.